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Structural-mechanical AFM study of inhomogeneous stiff nanocoating of softpolymer substrate

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Modification of polymer surfaces with low-energy gas plasma (nitrogen, argon, oxygen, acetylene) is used to change the wettability of the surface and, as a consequence, to control the interaction with biological objects [1]. As a result of such treatment, a carbonized surface nanolayer [2] is formed on a wide class of polymers. Polyurethane is one of the most widespread polymers. This is the two-phase material consisting of soft and stiff blocks. The structure and fraction of the hard phase depend on the recipe and manufacturing conditions. In this work, the soft elastic polyurethane (initial elastic modulus is 30 MPa) was studied; the stiff phase of which forms a percolation thread-like network (Fig. 1). The AFM indentation of this polymer showed heterogeneous surface stiffness up to the depth of 10 nm; at higher indentation depth the stiffness becomes homogeneous.

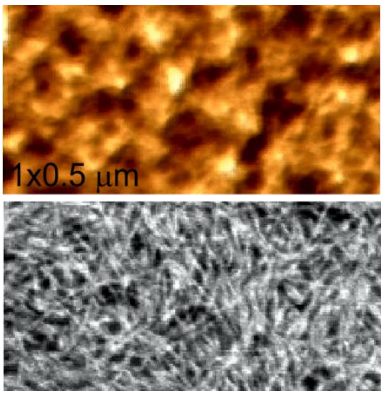

Figure 1. AFM images of relief and phase of the untreated polyurethane.

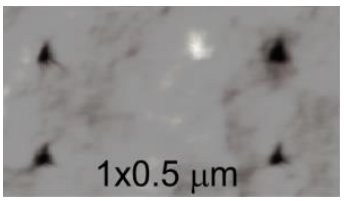

Figure 2. Indentation imprints of the treated surface.

Plasma treatment was performed in the vacuum chamber of the plasma unit. Argon and nitrogen partial pressures were set at $2 \cdot 10^{-3}$ Torr and a glow discharge with a current of 2 A was ignited in the source of a low-energy electron beam and an accelerating voltage of 100 V was set. Injection of electrons into the chamber provided generation of Ar-N_2 plasma, the particles of which interacted with the surface of the samples. Treatment time was regulated in the range of 0.5-2 minutes.

As a result of treatment, the surface acquires a rough granular structure. The obtained samples were indented with a probe with high spring constant of the cantilever and indentation imprints (Fig. 2) were observed on the surface. At the same time, the untreated polymer is recovered elastically after the similar indentation. Thus, the measured depth of the imprint was used to estimate the thickness of the hard layer (6-9 nm). The modified layer is locally inhomogeneous: its thickness depends on the surface area. The AFM study in force modulation regime established heterogeneous stiffness of the activated surfaces. The average value of stiffness increases with the treatment time, but the thickness of the layer increases to a certain limit and then does not change. All these features are related to the heterogeneous surface features of the initial polyurethane.

In addition to the structural-mechanical properties, the surface energy also changes (inversely proportional to the treatment time). Which, in turn, influences the sorption of blood proteins. The properties of such a heterogeneous stiff coatings must be taken into account when designing deformable products which surface could be damaged under certain loading conditions.

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